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A cluster heated and compressed by an impact at a surface has been studied as a medium for driving chemistry under controlled extreme conditions. The following aspects were examined: Is the temperature rise following impact sufficient to overcome high barriers to reactions; what is the range of impact velocities that is useful for this purpose; does the cluster retain enough of its integrity for a length of time sufficient that chemistry can take place within it; what is the role of electronically non-adiabatic processes; what is the mechanism of activation within the hot and compressed cluster; what is the mechanism for ionization in the hot cluster and in other very energy rich systems; can specific examples of cluster impact induced chemistry be provided. Detailed discussions of these questions are provided in published papers and in two reviews.

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ENERGY AND CHEMICAL CHANGE

AFOSR GRANT No. F49620-97-1-0215

Final Technical Report

By

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Program Manager: Dr. Michael R. Berman

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Objectives

The objective of this research effort is a theoretical and computational understanding of chemistry under extreme conditions (which is characteristic of many situations of direct interest to he Air Force) and/or to new experimental results for such processes.

Status of effort

The work had three main aspects: examining and understanding new phenomena, the role of electronic excitation and the more detailed examination of aspects that are broadly understood but deserve a second look. A technical overview is provided in the recent application submitted to AFOSR. Annual technical reports provided detailed reports as follows:

2001 Characterizing the high energy density/high material density stage during cluster impact. This work has just been accepted for publication but is not out yet. Below we provide a discussion of where we are now with this effort.

2000 Overview of cluster-impact induced chemistry.

1999 The formation of electronically excited products during cluster impact.

1998 The FMS methodology for computing dynamics on several electronic states.

1997 On a fast yet finite electronic time scale which underlies chemical reactions of electronically excited polyatomic species.

Current effort

As discussed in the technical report for 2001, there is a compression interlude during the cluster impact when it is very hot and dense and it thereby provides a suitable medium for driving high barrier chemical reactions. It is therefore natural to want to compute such obvious measures as the density of the cluster. We were not able to do so in a meaningful fashion because the cluster is very disordered on the one hand and the number of the atoms is small enough that it is not possible to partition the volume of the cluster into

regions where the density can be determined in a statistically significant way. Indeed, the packing is so irregular that it is not even clear what is 'the volume' of the cluster. Further, during the compression interlude the atoms are very close and strongly interacting so much so that a high fraction of the initially directed energy of impact is stored as potential energy of repulsion, While we thus have no good way to characterize the distribution of the cluster in (coordinate, that is physical) space, the distribution in momentum space is very well characterized: After an extremely short time it relaxes from initially a delta function to a Maxwell-Boltzmann (thermal) distribution.

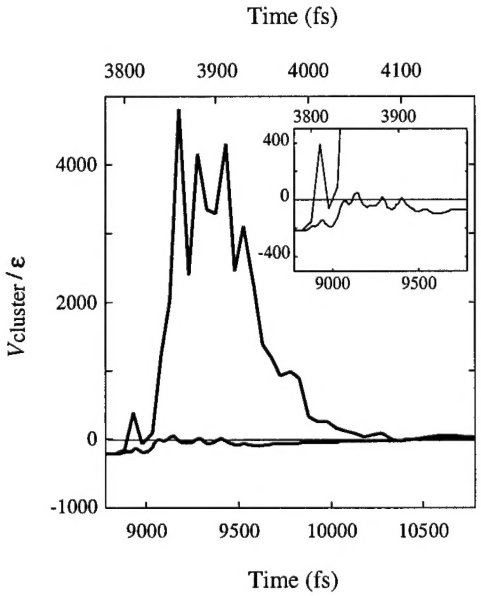
Given a very non ideal gas in thermal equilibrium, a statistical mechanician will present the distribution in coordinate space as a virial expansion (in powers of 1/volume). This will not work for us because the order of a term in the virial expansion equals the number of atoms that are interacting. In the compressed cluster many atoms are simultaneously interacting and the virial series will not converge.

So we asked 'where does the virial series come from? Maybe it can be summed exactly?' Indeed, the series has an exact sum as given by the long forgotten virial theorem. There is only one snag. The derivation of the virial theorem takes it as given that the gas is confined to a container of a given volume by the application of an external pressure and it is maintained in this way for a long time until it comes to equilibrium. All of this is exactly what is not the case for the cluster. There is no container and no external pressure and the whole interlude lasts only for a few hundred fs's, so a long time averaging, as employed in the derivation of the virial thoerem, is out of question.

The first obstacle was easy. It turns out that there is no real need for a long time averaging as usually done. It simplifies the derivation but it is not essential. So we derived an instantaneous virial theorem; a theorem that is valid at every instant in time. The second obstacle did not appear easy. Our cluster is evolving and technically what is problematic, it fragments. It is not confined to a container.

Sometime ago, with the support of AFOSR, we have developed a dynamical version of surprisal analysis. So we decided to apply it. We let the cluster evolve under the constraint of an external pressure. Once we do that there is a valid virial theorem and hence we can compute the product pressure·volume. This is where we are and we are

quite pleased. It is a new application of the dynamical version of surprisal analysis. On modern computers it is working so very well that we also plan to return to the old applications and see can we now implement it as a viable numerical approach. Before that however we plan to follow further the application to the hot and dense cluster.



The quantitative difference between supersonic, bottom time scale and hypersonic, top time scale, impacts. The total Ar-Ar potential energy, in units of the Ar-Ar potential well depth, during the compression. Before collision with the surface, each Ar atom has several near neighbors and the total potential energy is about -200ε, see insert. For supersonic impact, enough energy is provided to dissociate the cluster, (potential energy above zero), but not much more. For hypersonic impact, the compression is extreme. The average repulsion between two neighboring Ar atoms reaches as high as 20ε.

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